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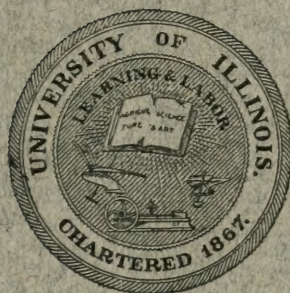
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ON THE RATE OF FORMATION OF CARBON MONOXIDE IN GAS PRODUCERS

BY

J. K. CLEMENT



UNIVERSITY OF ILLINOIS
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UNIVERSITY OF ILLINOIS

ENGINEERING EXPERIMENT STATION

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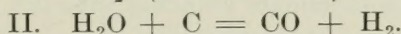
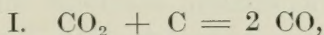
ON THE RATE OF FORMATION OF CARBON MONOXIDE IN GAS PRODUCERS

BY J. K. CLEMENT, PHYSICIST, U. S. G. S., TECHNOLOGIC BRANCH, ASSISTED BY
L. H. ADAMS, JUNIOR CHEMIST, U. S. G. S., TECHNOLOGIC BRANCH;
APPENDIX BY C. N. HASKINS, ASSISTANT PROFESSOR OF
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I. INTRODUCTORY STATEMENT.

The rapid advance in the use of producer gas in recent years has given rise to a demand for a more accurate knowledge of the processes taking place in the fuel bed of the producer and the effect on these processes of certain variations in the conditions of operation. The primary function of the gas producer is to transform solid fuel into a more readily combustible gaseous fuel. This transformation, which is relatively slow, consists of the following processes:

1. The distillation of the volatile hydro-carbons from the freshly fired fuel at relatively low temperatures.
2. The combustion of fuel by combination with the oxygen of the air.
3. The formation of producer gas proper in accordance with the equations:



The first of these reactions, the formation of carbon monoxide, is the one with which the present investigation deals. The problem proposed is in broad terms to determine the factors that govern the production of CO in the gas producer; and the effect of the temperature and of the time of contact of the gas and carbon on the percentage of CO in the producer gas. The question

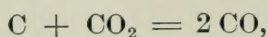
of the effect of temperature was brought forth by certain experiments made by one of the writers at the Fuel Testing Plant of the U. S. Geological Survey at the Jamestown Exposition, in which it was found that the temperature in the fuel bed of the gas producer varies greatly from one portion of the bed to another. In order, therefore, to ascertain the conditions of temperature most favorable to the efficient operation of the producer, it becomes necessary to determine the temperature requisite for the formation of carbon monoxide and hydrogen in accordance with the reactions quoted in the preceding paragraph.

A study of the conditions for the reduction of CO_2 by carbon seems desirable from another consideration. A small amount of CO is invariably contained in the flue gases of boiler furnaces. It was hoped, therefore, that the investigation might furnish an explanation of the formation of CO in boiler furnaces and perhaps suggest a means of preventing such formation.

The investigations herein described were made in, and with the facilities of, the Physical Laboratory of the University of Illinois.

II. FUNDAMENTAL EQUATIONS.

According to the law of chemical mass action, a chemical reaction, as for example the reaction expressed by the equation



proceeds in one direction until equilibrium is established and then stops; and when the system is in equilibrium there is for a given temperature a certain constant relation between the amounts of the components entering into the reaction. Thus, in the system under consideration, let

[CO] = the concentration of CO in gram molecules¹ per liter,
[CO₂] = the concentration of CO₂ in gram molecules per liter;
then for equilibrium, the relation

¹A gram molecule of a substance is a weight of the substance in grams numerically equal to the molecular weight. Thus a gram molecule of CO is 28 grams, one of CO₂ is 44 grams, etc.

$$\frac{[\text{CO}]^2}{[\text{CO}_2]} = \text{constant} = K \quad (1)$$

must be satisfied.

The relation (1) may be thrown into another form as follows:

Let 100 x = per cent of CO in the gas by volume;

100 $(1 - x)$ = per cent of CO_2 in the gas by volume;

p = pressure in atmospheres;

T = absolute temperature;

R = absolute gas constant = 0.0821 for the system of units here employed;

n = number of gram molecules of the gas under consideration;

v = volume of gas in liters.

The characteristic equation of gases is

$$pv = nRT$$

from which

$$\frac{n}{v} = \frac{p}{RT}$$

Now xn and $(1 - x)n$ are respectively the numbers of gram molecules of CO and CO_2 in the gas; hence the concentrations of CO and CO_2 are respectively

$$\begin{aligned} [\text{CO}] &= \frac{xn}{v} = \frac{xp}{RT} \\ [\text{CO}_2] &= \frac{(1 - x)n}{v} = \frac{(1 - x)p}{RT} \end{aligned}$$

Placing these values in (1), the resulting equation is

$$\frac{x^2}{1 - x} \frac{p}{RT} = K \quad (2)$$

If the pressure and temperature are kept constant, the factor

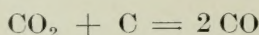
$\frac{p}{RT}$ is a constant, and (2) may be written

$$\frac{x^2}{1 - x} = \frac{KRT}{p} = K' \quad (3)$$

where K' is a new constant.

When CO_2 gas is maintained in contact with carbon at constant temperature and pressure the two will react rapidly at first and then more slowly until the amount of CO formed is 100 x per cent of the total, where x is given by equation (3).

The relation expressed by (1) may be considered as a special case of a more general law. According to the theory of the kinetics of reactions now generally accepted in reversible reactions, two reactions take place simultaneously, one from left to right and one from right to left. In the reaction



the velocity of the reaction from left to right, that is, the rate of formation of CO, is at any instant proportional to the number of CO_2 molecules in the unit volume; thus denoting the velocity by v ,

$$v = k_1 [\text{CO}_2].$$

Similarly the velocity of the reaction from right to left, that is, the rate of formation of CO_2 , is proportional to the square of the number of CO molecules in a unit volume. Hence

$$v' = k_2 [\text{CO}]^2$$

The increase in the number of CO molecules per unit volume in the time dt is the difference of the two velocities v and v' ; that is,

$$\frac{d[\text{CO}]}{dt} = v - v' = k_1 [\text{CO}_2] - k_2 [\text{CO}]^2 \quad (4)$$

As $[\text{CO}]$ the number of gram molecules of CO in the unit volume increases and $[\text{CO}_2]$ the number of gram molecules of CO_2 decreases, the velocity $\frac{d[\text{CO}]}{dt}$ will become smaller and smaller until finally $[\text{CO}]$ and $[\text{CO}_2]$ become constant, that is, the system attains equilibrium. In this case we have, therefore,

$$\frac{d[\text{CO}]}{dt} = v - v' = 0$$

whence

$$k_1 [\text{CO}_2] = k_2 [\text{CO}]^2. \quad (5)$$

That is, the number of CO_2 molecules formed in a given time is equal to the number that are decomposed to form CO. The last equation may be written

$$\frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{k_1}{k_2} = K. \quad (6)$$

K is called the *equilibrium constant*.

Equation (4) giving the rate of formation of CO may be modified as follows:

Let $100 a =$ per cent of CO_2 by volume at the beginning of the reaction, that is, when $t = 0$,

$100 x =$ per cent of CO by volume after the time t has elapsed.

At the beginning of the reaction, that is when $t = 0$, there is no CO, hence $x = 0$. If now n is the number of gram molecules of the gas when $t = 0$, then na is the number of gram molecules of CO_2 , and the concentration of the CO_2 is therefore

$$[\text{CO}_2] = \frac{n a}{v}.$$

But since $pv = n R T$, this relation may be written

$$[\text{CO}_2] = \frac{a p}{R T} = M \text{ gram molecules per liter.}$$

At the time t suppose m gram molecules per liter of CO to have been formed. This involves the disappearance of $\frac{m}{2}$ gram molecules per liter of CO_2 , leaving $M - \frac{m}{2}$. The number of gram molecules of gas is now

$$\begin{aligned} n(1-a) + \left[M - \frac{m}{2} + m \right] v \\ = n(1-a) + \left(M + \frac{m}{2} \right) \frac{n a}{M} \end{aligned}$$

$$= n \left(1 + \frac{m a}{2 M} \right)$$

$$= n \left(1 + \frac{m}{2} \frac{RT}{p} \right),$$

and the volume of the gas is therefore increased from v to $v \left(1 + \frac{m}{2} \frac{RT}{p} \right)$. The concentrations at the time t are therefore

$$[\text{CO}] = \frac{m}{1 + \frac{m}{2} \frac{RT}{p}}, \quad (7)$$

$$[\text{CO}_2] = \frac{M - \frac{m}{2}}{1 + \frac{m}{2} \frac{RT}{p}}. \quad (8)$$

But since 100 x per cent of the gas is CO by volume the concentration of the CO is also given by the relation

$$[\text{CO}] = \frac{xp}{RT}. \quad (9)$$

Combining the two expressions for $[\text{CO}]$ given by (7) and (9), we obtain.

$$m = \frac{2x}{2-x} \frac{p}{RT},$$

and introducing this expression for m in (8), the result after slight reduction is

$$[\text{CO}_2] = \left(a - \frac{a+1}{2} x \right) \frac{p}{RT}. \quad (10)$$

Introducing in equation (4) the expressions for the concentrations given by (9) and (10), the result is

$$\frac{d[\text{CO}]}{dt} = k_1 \frac{p}{RT} \left(a - \frac{a+1}{2} x \right) - k_2 \left[\frac{p}{RT} \right]^2 x^2. \quad (11)$$

But from (9)

$$\frac{d[\text{CO}]}{dt} = \frac{p}{RT} \frac{dx}{dt},$$

whence

$$\frac{dx}{dt} = k_1 \left(a - \frac{a+1}{2} x \right) - k_2 \frac{p}{RT} x^2.$$

Replacing the constant $k_2 \frac{p}{RT}$ by a single symbol k'_2 , the final equation for the reaction velocity is

$$\frac{dx}{dt} = k_1 \left(a - \frac{a+1}{2} x \right) - k'_2 x^2. \quad (12)$$

The integration of the differential equation (12) offers no great difficulty.

The determination of the constants k_1 and k_2 seems to have been made hitherto by assuming the value of the ratio $\frac{k_1}{k'_2}$. This

method is applicable when the equilibrium conditions are readily realized. As, however, this is not the case in the present reaction it has been necessary to devise a method for the determination of k_1 and k'_2 from two or more pairs of simultaneous observations of x and t . It turns out that the method is applicable not only to the reaction in question, but also to the most general incomplete reactions of the second order.

The great difficulty of realizing, with certainty, the condition of the equilibrium in reactions like the one under consideration, makes it highly desirable, therefore, to obtain a general solution of the differential equation, without introducing a particular numerical

value for the ratio $\frac{k_1}{k'_2}$. We are indebted to Prof. C. N.

Haskins for the following solution, the developments of which will be found in the appendix:

$$x = \frac{4a}{a+1} \frac{\gamma \tanh at}{1 + \gamma \tanh at}. \quad (13)$$

In equation (13) a and γ are determined by the relation

$$k_1 = \frac{4a\gamma}{a+1},$$

$$k'_2 = \frac{a(a+1)}{4a\gamma} (1 - \gamma^2).$$

When the initial percentage of CO_2 is 100, then $a = 1$,

$$\frac{dx}{dt} = k_1 (1 - x) - k'_2 x^2,$$

and

$$x = \frac{2\gamma \tanh at}{1 + \gamma \tanh at} \quad (14)$$

In the case of the gas producer the value of a is about 0.21.

III. BOUDOUARD'S EXPERIMENTS.

An elaborate series of determinations of the amount of CO formed at different temperatures has been made by O. Boudouard.¹ Boudouard's observations were made at 650°, 800° and 925° C. In his experiments at 650° and 800° glass tubes containing charcoal, coke, retort carbon or lamp black were filled with CO_2 , heated to the temperature of the experiment and then sealed. The tubes were maintained at constant temperature until equilibrium was reached, that is, when further heating at the same temperature produced no increase in the percentage of CO present. At 650° the heating was continued for twelve hours before equilibrium was attained. At 800° equilibrium was reached in one hour in the tubes containing charcoal and in two and one-half hours in those containing lamp black. With coke and retort carbon the process was not complete at the end of nine hours. In the experiment at 925° the carbon was heated in a porcelain tube, through which was passed a stream of CO_2 gas. The average time of contact between CO_2 and carbon calculated from the data given

¹O. Boudouard, *Comptes Rendus de l'Academie des Sciences*,

Vol. 128, page 824, 154; 1899.

Vol. 131, page 1204, 1900.

Vol. 130, page 132, 1900.

Bulletin Soc. Chim., Paris, Vol. 21, 1901.

Bulletin Soc. Chim., Paris, Vol. 25, 1901.

Ann. de Chimie et de Physique, Vol. 354, 1901.

See also Haber, *Thermodynamics of Technical Gas Reactions*, 1908, p. 311.

in Boudouard's account of his experiments was approximately 30 seconds.

A summary of Boudouard's results is given in the following table:

TEMPERATURE C. ^o	PER CENT OF CO ₂	PER CENT OF CO
650.	61.	39.
800.	7.	93.
925.	4.	96.

These values have been made the basis of computation by many writers on the chemistry of combustion and of the water gas reaction and especially in treatises on the gas producer.

In the first references to Boudouard's work which came to the attention of the writers, no notice was taken of the remarkably low reaction velocity of the formation of CO from CO₂ and carbon, and of the great length of time required to obtain the percentages of CO that are given in the preceding table. In at least one case the values shown above were offered as representing the quality of gas that should be obtained in the gas producer at the temperatures given. The writers were therefore led to regard Boudouard's figures as defining the relative proportions of CO₂ and CO that should be formed in a gas producer at various temperatures of the fuel bed.

The experiments which form the subject of this paper had originally as their object the confirmation of Boudouard's results as well as a continuation of them at higher temperatures. Preliminary experiments made by Dr. C. S. Hudson demonstrated that the amount of CO formed at a given temperature depends largely on the time of contact or in other words on the rate of flow of the gas through the fuel bed. Apparently Boudouard's results represent limiting values, which can be obtained only with a very low gas velocity. In order to ascertain the conditions for the formation of CO in producer furnaces, it is necessary, therefore, to determine the rate of formation of CO from CO₂ and carbon at various temperatures; that is, to determine the

amount of CO formed with different rates of flow of the gas through the fuel bed.

IV. METHOD OF EXPERIMENT.

The arrangement of the apparatus is shown in Fig. 1, 2, and 3. A porcelain tube of 1.5 cm inside diameter, 60 cm long, and glazed on the outside was filled with charcoal, coal, or coke and heated in an electric furnace. The furnace, which was designed

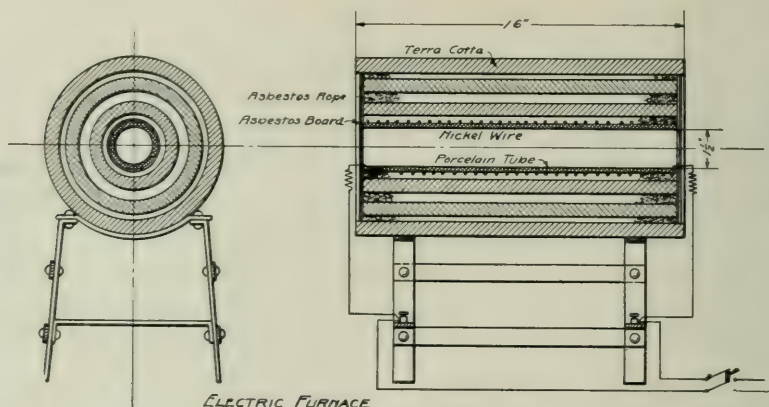


FIG. 1

especially for this investigation, is shown in detail in Fig. 3. It has been operated continuously for a period of six months at temperatures of from 800° to 1200° , and even 1300° C. The temperature inside the porcelain tube could be maintained at any value up to 1300° C with no fluctuations greater than 1° or 2° . The



FIG. 2

heating coil consists of a coil of No. 13 nickel wire, wound with eight turns per inch on an electrical porcelain insulating tube of 38 mm inside diameter and 35 cm long. At either end of the coil

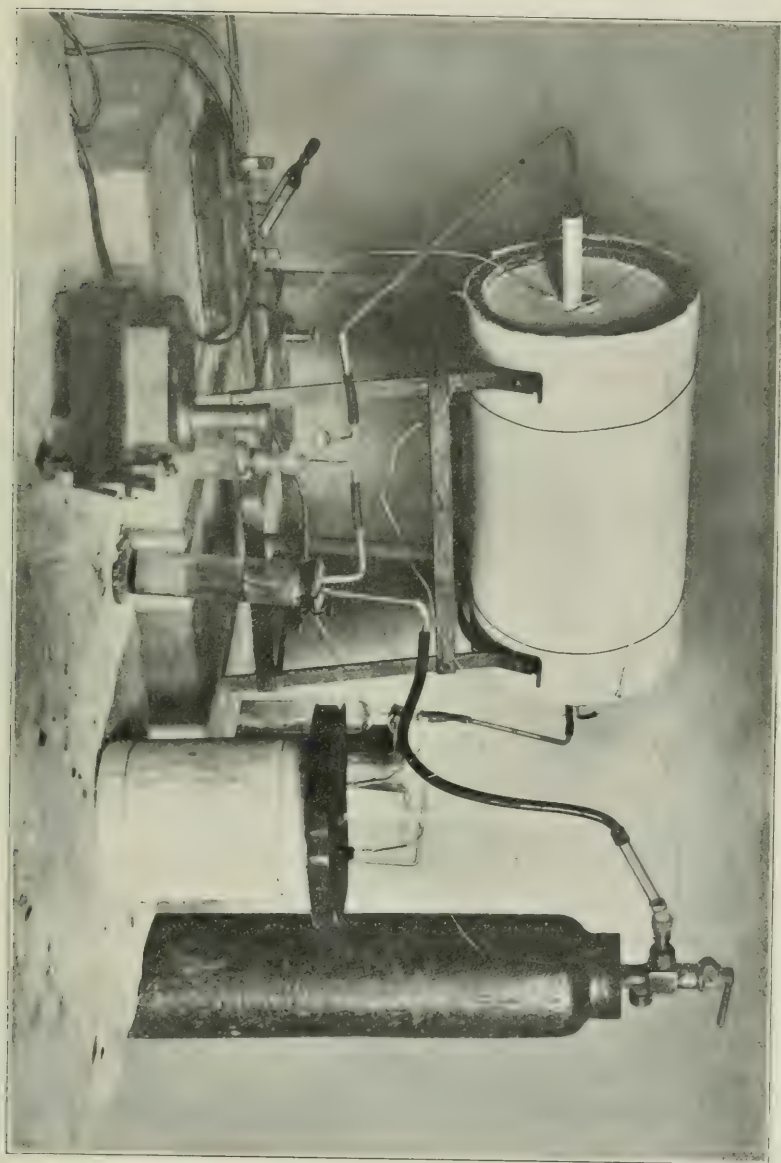


Fig. 3

the number of turns was increased slightly to compensate for the cooling effect of the end at the furnace. As a protection against corrosion, the coil was painted over with a thin layer of magnesite cement—a material that is capable of withstanding very high temperatures. The heating tube was then mounted inside of and concentric with several terra cotta pipes and the spaces between the pipes were filled with light calcined magnesia. The cost of the material used in the furnace and the amount of labor required were very small. A temperature of 1000°C could be maintained by the expenditure of 600 watts.

The temperature inside the porcelain tube was measured by means of a platinum platinum-rhodium thermocouple (see Fig. 2) and a Siemens & Halske milli-voltmeter. As the thermo-electric height of the couple fell slightly with use at high temperature—due probably to the reducing action of CO gas on the insulating tubes and the consequent contamination of the couple—it was found necessary to calibrate the couple from time to time. This was accomplished by determination of the melting points of zinc, silver and copper. The error of individual temperature observations does not exceed 5° below 1100° and 10° to 15° between 1100° and 1300° .

The carbon with which the porcelain tube was filled was crushed to pieces of a uniform size—about 5 mm on a side. Only the central portion of the tube (see Fig. 2) contained carbon, the remainder of the space being occupied by pieces of broken porcelain, which served at one end to heat the gas entering the tube, and at the other end, by reducing the size of the passage way, to increase the velocity of the gas through the region of falling temperature. Through the porcelain tube was passed a stream of CO_2 gas. In the earlier experiments CO_2 was prepared from marble and hydrochloric acid. Later, CO_2 was taken from a tank of liquid carbon dioxide.

The velocity of the gas over the carbon was determined by the dimensions of the tube, the weight and density of the carbon,

and the temperature and the volume of gas passed through the tube per minute.¹

The analyses were made by the Hempel method, both CO₂ and CO being absorbed. The amount of gas remaining in the burette after the absorption in cuprous chloride was seldom greater than two per cent.

V. EXPERIMENTS WITH CHARCOAL.

With the apparatus described in the preceding pages, experiments were conducted at temperatures ranging from 700° to 1300° C. The experiments with charcoal extended over a period of several months. The results are contained in tables 1-6.

TABLE 1
RATE OF FORMATION OF CO FROM CO₂ AND CHARCOAL
AT A TEMPERATURE OF 800° C.

$$k_1 = 0.01968$$

$$k_2 = 3.031$$

Time of contact in seconds <i>t</i>	<i>l</i>	% CO 100 Observed	% CO 100 Calculated
∞	0		0.535
188.6	0.0053	0.503	0.534
115.9	0.0086	0.504	0.527
57.18	0.0175	0.518	0.508
45.70	0.0219	0.522	0.468
24.20	0.0413	0.375	0.345
15.50	0.0645	0.283	0.252
12.32	0.0810	0.245	0.209
2.686	0.354	0.063	0.051
1.550	0.645	0.039	0.030

¹The increase in the volume of the gas in its passage through the reaction tube, due to the formation of two CO molecules in place of every molecule of CO₂ which disappears, makes it difficult to determine accurately the time of contact and consequently the velocity of the gas.

The values of *t*, the time of contact, given in the following tables are based on the volume of gas leaving the tube and are therefore somewhat too low. Since the major portion of the expansion takes place within a short distance from the entrance to the tube, the error here introduced is probably not appreciable.

TABLE 2

RATE OF FORMATION OF CO FROM CO₂ AND CHARCOAL

AT A TEMPERATURE OF 850° C.

$$k_1 = 0.07174$$

$$k_2 = 3.238$$

Time of contact in seconds t	$\frac{1}{t}$	% CO 100 Observed	% CO/100 Calculated
∞	0		0.742
123.0	0.0082	0.743	0.742
54.18	0.0184	0.702	0.741
24.43	0.0410	0.572	0.694
13.13	0.0756	0.526	0.564
9.268	0.1070	0.297	0.463
4.630	0.216	0.297	0.281
3.684	0.271	0.224	0.231
3.254	0.307	0.225	0.207

TABLE 3

RATE OF FORMATION OF CO FROM CO₂ AND CHARCOAL

AT A TEMPERATURE OF 900° C.

$$k_1 = 0.1540$$

$$k_2 = 2.599$$

Time of contact in seconds t	$\frac{1}{t}$	% CO 100 Observed	% CO/100 Calculated
∞	0		0.873
64.29	0.0156	0.873	0.873
41.18	0.0226	0.867	0.872
10.008	0.0999	0.708	0.739
4.257	0.234	0.498	0.472
2.840	0.352	0.311	0.351
2.172	0.461	0.344	0.284

TABLE 4

RATE OF FORMATION OF CO FROM CO₂ AND CHARCOAL

AT A TEMPERATURE OF 925° C.

$$k_1 = 0.2175$$

$$k_2 = 2.298$$

Time of contact in seconds t	$\frac{1}{t}$	% CO 100 Observed	% CO/100 Calculated
∞	0		0.914
118.8	0.0084	0.947	0.914
81.2	0.0123	0.933	0.914
12.37	0.0807	0.848	0.875
5.80	0.1725	0.718	0.697
4.277	0.234	0.642	0.595
2.272	0.440	0.375	0.387

TABLE 5

RATE OF FORMATION OF CO FROM CO₂ AND CHARCOAL

AT A TEMPERATURE OF 1000° C.

$$k_1 = 0.6404$$

$$k_2 = 4.708$$

Time of contact in seconds t	$\frac{1}{t}$	% CO/100 Observed	% CO/100 Calculated
∞	0		0.942
70.0	0.0143	0.949	0.942
18.60	0.0538	0.943	0.941
8.245	0.1195	0.903	0.938
3.675	0.272	0.797	0.869
2.296	0.436	0.795	0.752

TABLE 6
RATE OF FORMATION OF CO FROM CO₂ AND CHARCOAL
AT A TEMPERATURE OF 1100° C.

$$k_1 = 1.495$$

$$k_2 = 5.275$$

Time of contact in seconds t	$\frac{1}{t}$	% CO 100 Observed	% CO/100 Calculated
∞	0		0.972
36.48	0.0274	0.987	0.972
10.43	0.0958	0.983	0.972
4.968	0.2010	0.981	0.971
3.640	0.2745	0.973	0.968
1.921	0.521	0.946	0.955

The first and second columns of each table give the time of contact t and the reciprocal of the time of contact $\frac{1}{t}$, which is equal to the velocity of the gas divided by the length of the charcoal column; thus

$$\frac{1}{t} = \frac{v}{l}.$$

The third column contains the percentages of CO observed, and the values in the last column were calculated by means of equation (13), viz:

$$x = \frac{4a}{a+1} \frac{\gamma \tanh at}{1 + \gamma \tanh at}$$

The method of computing a and γ of this equation is described in the appendix. The constants k_1 and k'_2 are determined by the relations,

$$k_1 = \frac{4a\gamma}{a+1}$$

$$k'_2 = \frac{a(a+1)}{4a\gamma} (1 - \gamma^2)$$

Values of k_1 , k_2 , k'_2 , a , and γ are given in table 7.

TABLE 7
CONSTANTS USED IN COMPUTATION OF x

Temp. C°	a ($a = 1$)	γ ($a = 1$)	k'_2	k_2	k_1	$K = \frac{k_1}{k_2}$
800.	0.0276	0.3568	0.03373	3.031	0.01968	0.006493
850.	0.0612	.5853	0.03443	3.238	0.07174	0.02216
900.	0.09998	.7711	0.02646	2.599	0.1540	0.05925
925	0.1297	.8388	0.02291	2.298	0.2175	0.09465
1000	0.3617	.8853	0.04416	4.708	0.6404	0.13603
1100	0.7921	.9437	0.04588	5.275	1.4950	0.28341

The calculated and observed values of x , the per cent of CO, agree within two or three per cent.

A comparison of the results in tables 1 to 6 shows in the first place that with increasing temperature there is a rapid increase in the percentage of CO obtained with any given rate of

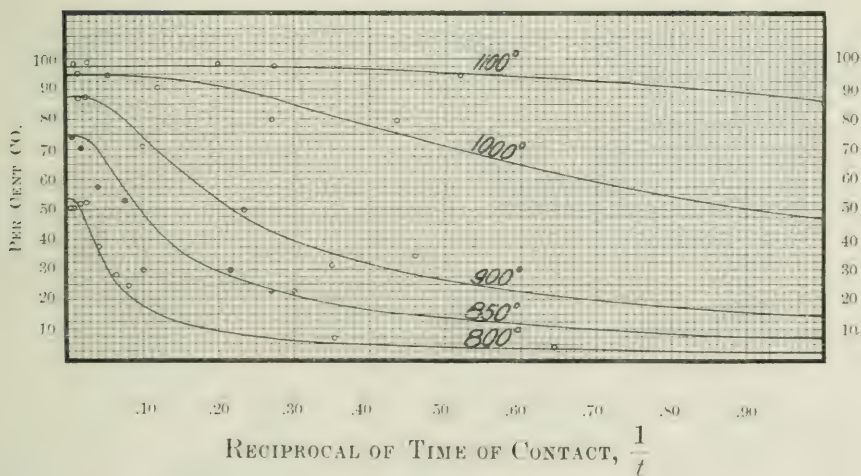


FIG. 4.

flow of the gas; in the second place that with increasing gas velocity at low temperatures the percentage of CO formed falls off very rapidly, at higher temperatures very slowly. These variations are illustrated by the curves in Fig. 4 in which the per-

centage of CO is plotted as a function of $\frac{1}{t} = \frac{v}{l}$. When l , the length of the charcoal column, is equal to one, i. e., is equal to the unit of length, then the numbers along the abscissa give the velocity of the gas in terms of the same unit of length, and per second. For example, the length of the charcoal column in the experiments here recorded, was approximately 20 cm. The velocity corresponding to the point $\frac{1}{t} = 1$ at the extreme right of Fig. 4, is therefore 20 cm. per second.

The general shape of all the curves in Fig. 4 is the same. The percentage of CO is greatest at zero velocity. With increasing values of $\frac{1}{t}$ each curve falls off, slowly at first then more rapidly, passing a point of inflection and finally becoming nearly horizontal. The intersections of the curves with the CO axis give the percentage of CO corresponding to the condition of equilibrium.

That a considerable amount of time is required to reach equilibrium in the reaction under consideration, is further illustrated in Fig. 5, in which the percentage of CO is plotted as a function of t , the time of contact. (One small division = 1 second). At 800° for example, the percentage of CO reaches a practically constant value at the end of 50 sec.; at 1000° in 6 sec.

The curves in Fig. 4 were plotted from values of x (= per cent CO) calculated from equation (13). The observed values are indicated by the small circles. By means of equation (13) it is possible to calculate the per cent of CO corresponding to any given gas velocity providing α and γ or k_1 and k_2 are known.

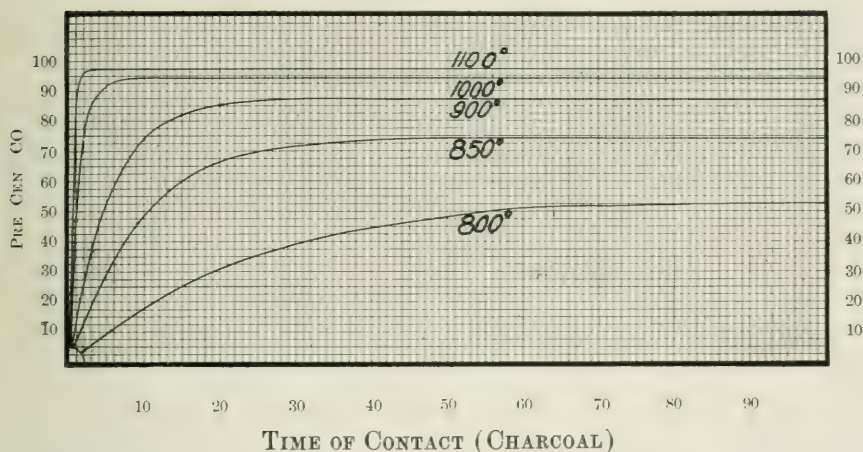


FIG. 5.

VI. VARIATIONS OF K AND k_1 WITH TEMPERATURE.

The values of k_1 and K given in table 7 exhibit a systematic variation with temperature. If equations can be found that will express k_1 and K as functions of the temperature it will then be possible to calculate the per cent of CO for any time of contact and any desired temperature. Such equations have been deduced by Van't Hoff from purely thermodynamical considerations. They are the following.¹

$$\frac{d(\ln K)}{dT} = - \frac{Q}{R T^2}, \quad (15)$$

and

$$\frac{d(\ln k_1)}{dT} = \frac{A}{T^2} + B. \quad (16)$$

In these equations, Q is the latent heat of reaction at the absolute temperature T , A is a function of Q but is selected arbitrarily, and B is an arbitrary function of the temperature. By integration the latter equation becomes

¹The symbol $\ln$ in the following equations stands for natural logarithm.

$$\ln k_1 = -\frac{A}{T} + B T + C, \quad (17)$$

where C is an integration constant. The values of A , B , and C , in equation (5) have been determined from the simultaneous values of k_1 and T of tables 1-6. Table 8 contains the values of k_1 , obtained at various temperatures as well as the values of k_1 calculated from equation (17). The agreement is remarkable good.

TABLE 8

VARIAION OF k_1 WITH TEMPERATURE (CHARCOAL)

$$\ln k_1 = -\frac{50910}{T} - 0.0203 T + 65.376$$

Temp. Deg. C.	Absolute Temp. T	k_1 (obs)	k_1 (calc)
800	1073	0.020	0.021
850	1123	0.073	0.064
900	1173	0.154	0.159
925	1198	0.217	0.237
1000	1273	0.640	0.629
1100	1373	1.490	1.53

In order to integrate the equation

$$\frac{d(\ln K)}{dT} = -\frac{Q}{RT^2}$$

it is first necessary to determine the heat Q as a function of the temperature. It has been shown by Kirchoff that the increase of Q per degree rise in temperature is equal to the difference of the molecular heats of the factors and of the products of the reaction. Following this law, and taking the specific heat of a factor or product as a linear function of the temperature, which is very nearly true for gases, the relation between Q and T is given by the equation¹

$$Q = Q_0 + c_1 T + c_2 T^2 \quad (18)$$

In this equation Q_0 denotes the heat of reaction for $T = 0$, and c_1 and c_2 are obtained as follows: Assuming that the mean specific heat of each gas is given by an expression of the form

¹Haber, *Thermodynamics of Technical Gas Reactions*, p. 49, eq. (7a).

$$c = a + b T,$$

then c_1 is the difference between the sum of the a 's of the factors and the sum of the a 's of the products; likewise c_2 is the sum of the b 's of the factors less the sum of the b 's for the products. Substituting the value of Q given by (18) in (15) the result is

$$\frac{d(\ln K)}{dt} = -\frac{1}{R} \left(\frac{Q_0}{T^2} + \frac{c_1}{T} + c_2 \right)$$

whence by integration

$$\ln K = \frac{1}{R} \left(\frac{Q_0}{T} - c_1 \ln T - c_2 T \right) + C. \quad (19)$$

The constants in this equation, (19), may be determined by either of two different methods: by experimental determinations of Q_0 , c_1 , and c_2 , or from four or more simultaneous observations of K_{obs} and T . The first method was adopted in this instance, the following being the values of the quantities in question:

$$\begin{aligned} Q_0 &= -40166 \\ c_1 &= -2.055 \\ c_2 &= 0.003104 \\ C &= 8.604 \end{aligned}$$

In the determination of c_1 and c_2 , Langen's values for the specific heats of CO and CO₂ and the value of Kunz for the specific heat of charcoal were employed.

The value of R (in gram-calories per deg.) is 1.985. Hence taking the above constants and this value of R , (19) reduces to

$$\ln K = -\frac{20235}{T} + 1.035 \ln T - 0.001564 T + 8.604. \quad (20)$$

Table 9 gives values of K calculated from equation (20) along with values (marked K_{obs}) obtained from observed values of x and T in tables 1-6. In the fourth column are the observed values of x , the amount of CO in equilibrium with CO₂ and charcoal at temperatures from 800° to 1100°; and in the fifth columns the values of x corresponding to the values of K in the third column.

The constants of equation (19) were calculated also by the method of least squares, from simultaneous values of K_{obs} and T , but the agreement was less satisfactory than by the first method.

TABLE 9
VALUES OF K AND OF x_{∞}

Temp. C.	K (obs)	K (cal)	x_{∞} (obs)	x_{∞} (cal)	x_{∞} (obs) Boudouard
500		0.000007		0.021	
600		0.00013		0.093	
650		0.00046		0.185	0.39
700		0.00137		0.283	
800	0.0065	0.0090	0.526	0.582	0.93
850	0.022	0.020	0.738	0.722	
900	0.059	0.042	0.871	0.832	
925	0.094	0.060	0.912	0.873	0.96
1000	0.136	0.151	0.939	0.945	
1100	0.283	0.448	0.971	0.981	
1200		1.120		0.994	
1300		2.455		0.997	
1400		4.826		0.9985	
1500		8.671		0.9992	
1600		14.44		0.9996	

The agreement between "observed" and "calculated" values of K and k_1 in tables 8 and 9 shows that the changes of K and k_1 , with temperature follow van't Hoff's laws. It is possible, therefore, by means of equations (17) and (19) and the values of the constants of these equations given in tables 8 and 9, to compute K and k_1 for any desired temperatures. Having the values of K and k_1 and consequently of k_2 ($k_2 = \frac{k_1}{K}$) the per cent x of CO corresponding to any time of contact t can then be calculated by means of equation (13).

VII. EXPERIMENTS AT 700°.

In Fig. 4 the curve for 800° falls off very rapidly with increasing rate of flow of gas. At this temperature the gas velocity must be exceedingly low to obtain the equilibrium percentage of CO.

At temperatures below 800° it was practically impossible to reach equilibrium with a finite gas velocity. A great number of experiments were made at 700° but the results were too inconsistent to admit of mathematical treatment. Some of the observations are given in the following table:

TABLE 10
OBSERVATIONS AT 700° C. (CHARCOAL).

t = Time of contact in seconds	$\frac{1}{t}$	% CO 100
86.9	0.0115	0.012
86.2	0.0116	0.155
99.9	0.0100	0.077
23.4	0.0426	0.004
15.0	0.0668	0.014
7.11	0.1405	0.009
9.71	0.103	0.022
5.60	0.178	0.006
5.02	0.199	0.008
4.18	0.239	0.012

These results show that, except at exceedingly low velocities, the amount of CO formed was never greater than one or two per cent.

VIII. EXPERIMENTS WITH COKE AND COAL.

The experiments with coke and coal were conducted in the same manner as with charcoal. The material was crushed to pieces about 5 mm on a side. The constants α and γ of equation (13) were obtained for each temperature by the method given in the appendix. Tables 11-15 contain the results of the observations with coke. In the last column of each table are given the values of x , the percentage of CO formed, calculated from equation (13).

TABLE 11

RATE OF FORMATION OF CO FROM CO₂ AND COKE

AT A TEMPERATURE OF 900° C.

$$k_1 = 0.00231$$

$$k_2 = 0.03686$$

Time of contact in seconds. t	$\frac{1}{t}$	% CO/100 Observed	% CO/100 Calculated
142.0	0.0070	0.276	0.278
80.20	0.0124	0.131	0.169
43.91	0.0228	0.094	0.096
24.82	0.0403	0.057	0.056
16.11	0.0620	0.049	0.037
9.575	0.1045	0.026	0.023
3.741	0.2671	0.008	0.009

TABLE 12

RATE OF FORMATION OF CO FROM CO₂ AND COKE

AT A TEMPERATURE OF 1000° C.

$$k_1 = 0.02323$$

$$k_2 = 0.3591$$

Time of contact in seconds t	$\frac{1}{t}$	% CO/100 Observed	% CO/100 Calculated
123.2	0.0081	0.784	0.866
80.25	0.0125	0.644	0.795
33.25	0.0301	0.529	0.527
18.72	0.0535	0.320	0.350
6.37	0.1571	0.139	0.138
4.101	0.2439	0.115	0.091
3.072	0.3258	0.092	0.069
1.983	0.5045	0.063	0.045

TABLE 13

RATE OF FORMATION OF CO FROM CO₂ AND COKE

AT A TEMPERATURE OF 1100° C.

$$k_1 = 0.1335$$

$$k_2 = 0.5296$$

Time of contact in seconds t	$\frac{1}{t}$	% CO 100 Observed	% CO/100 Calculated
90.00	0.0111	0.971	0.971
29.92	0.0334	0.854	0.955
13.20	0.0758	0.661	0.817
6.765	0.1476	0.556	0.592
3.198	0.3135	0.317	0.346
1.784	0.5606	0.304	0.211
1.660	0.6030	0.240	0.1942
1.590	0.6299	0.221	0.190
1.462	0.6840	0.214	0.177
0.962	1.0399	0.133	0.121

TABLE 14

RATE OF FORMATION OF CO FROM CO₂ AND COKE

AT A TEMPERATURE OF 1200° C.

$$k_1 = 0.4095$$

$$k_2 = 0.6718$$

Time of contact in seconds t	$\frac{1}{t}$	% CO/100 Observed	% CO 100 Calculated
18.92	0.0528	0.989	0.987
12.70	0.0788	0.978	0.983
8.250	0.1213	0.953	0.956
2.402	0.4160	0.685	0.624
1.582	0.6320	0.439	0.460
1.080	0.9260	0.335	0.357

TABLE 15
RATE OF FORMATION OF CO FROM CO₂ AND COKE
AT A TEMPERATURE OF 1300° C.

$$k_1 = 1.483$$

$$k_2 = 0.7313$$

Time of contact in seconds t	$\frac{1}{t}$	% CO/100 Observed	% CO/100 Calculated
8.860	0.1129	0.999	0.997
4.149	0.2415	0.979	0.997
2.100	0.4760	0.932	0.955
1.130	0.8850	0.834	0.816

The results with coke are shown graphically in Fig. 6. The curves for 900°, 1000° and 1100° are considerably lower than the curves with charcoal for the same temperatures, except for very low velocities.

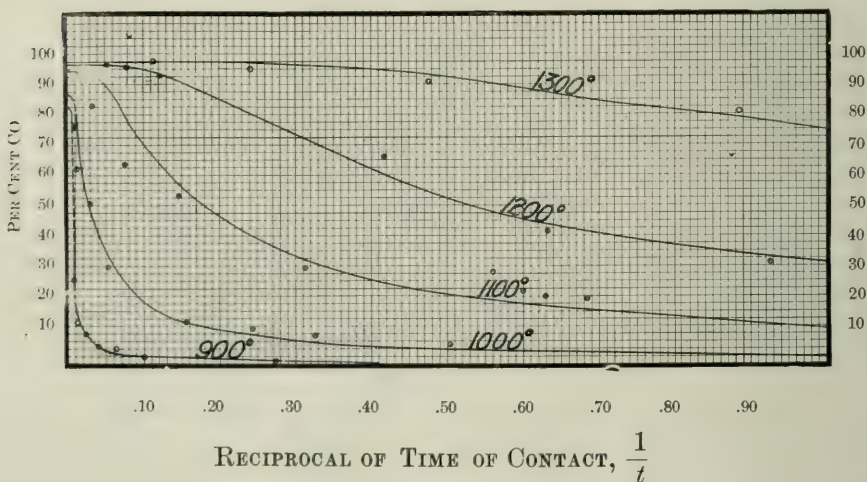


FIG. 6.

TABLE 16

RATE OF FORMATION OF CO FROM CO₂ AND ANTHRACITE COAL

AT A TEMPERATURE OF 1100° C.

$$k_1 = 0.119$$

$$k_2 = 1.410$$

Time of contact in seconds t	$\frac{1}{t}$	% CO 100 Observed	% CO 100 Calculated
34.20	0.0293	0.8780	0.912
9.370	0.1069	0.6010	0.657
5.415	0.1848	0.4770	0.472
3.301	0.3026	0.3020	0.322
2.439	0.4101	0.2650	0.251

TABLE 17

RATE OF FORMATION OF CO FROM CO₂ AND ANTHRACITE COAL

AT A TEMPERATURE OF 1200° C.

$$k_1 = 0.2374$$

$$k_2 = 0.1767$$

Time of contact in seconds t	$\frac{1}{t}$	% CO/100 Observed	% CO/100 Calculated
47.05	0.0212	0.997	0.993
10.39	0.0964	0.856	0.901
5.070	0.1971	0.715	0.688
2.845	0.3516	0.423	0.472
1.592	0.6270	0.310	0.309

TABLE 18

RATE OF FORMATION OF CO FROM CO₂ AND ANTHRACITE COAL

AT A TEMPERATURE OF 1300° C.

$$k_1 = 0.5791$$

$$k_2 = 0.2016$$

Time of contact in seconds t	$\frac{1}{t}$	% CO/100 Observed	% CO/100 Calculated
12.40	0.0806	0.999	0.997
6.030	0.1659	0.965	0.968
3.600	0.2779	0.824	0.876
2.980	0.3358	0.809	0.822
1.908	0.5249	0.663	0.668
1.070	0.9350	0.503	0.462

The observations with anthracite coal are given in tables 16, 17, and 18, and are illustrated graphically in Fig. 7.

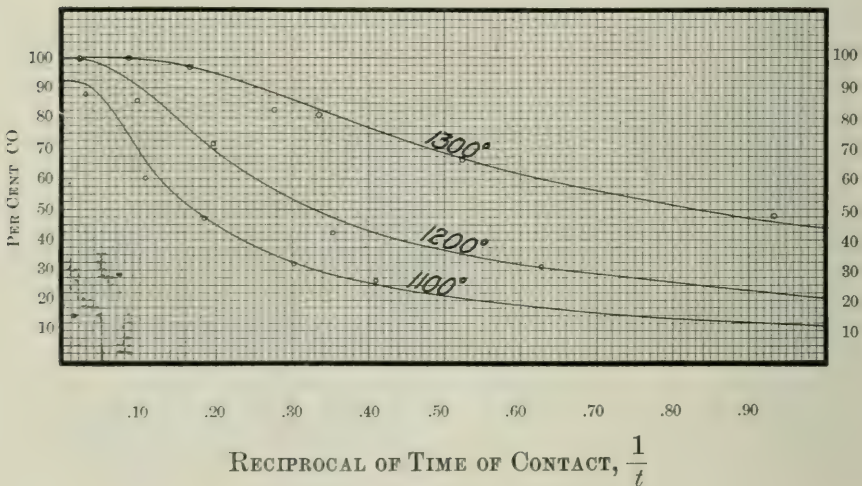


FIG. 7.

Here the curves fall off even more rapidly than the curves for coke in Fig. 6. With very low velocities, that is, when the time

of contact is sufficient for the reaction to reach equilibrium, the percentage of CO formed is practically the same with each of the three forms of carbon. As the rate of flow of the gas increases, the effect of the difference in the reaction velocities becomes more appreciable.

TABLE 19
VALUES OF x_{∞} FOR CHARCOAL, COKE, AND COAL.

Temp. C.	x_{∞} (cal)	x_{∞} (obs) Charcoal	x_{∞} (obs) Coke	x_{∞} (obs) Coal
900	0.832	0.871	0.875	
1000	0.945	0.939	0.886	
1100	0.981	0.971	0.968	0.914
1200	0.994		0.987	0.994
1300	0.997		0.996	0.997

Values of x_{∞} the percentages of CO in equilibrium with CO₂, and charcoal, coke, and coal respectively, are given in table 19. The values in the second column of this table were calculated from the values of K in table 9, by means of the equation

$$\frac{x^2}{1-x} = K \frac{RT}{p},$$

A comparison of Fig. 5, 6, and 7 shows that the reaction velocity is greatest with charcoal and lowest with anthracite coal. The temperature coefficient of k_1 , the coefficient of reaction velocity, was determined for coal and coke in the same manner as for charcoal. The "observed" and "calculated" values of k_1 are shown in tables 20 and 21.

The constant k_2 in the equation

$$\frac{d[\text{CO}]}{dt} = k_1 [\text{CO}_2] - k_2 [\text{CO}]^2$$

is the coefficient of reaction velocity of the reaction



taken from right to left. At the temperatures of these experiments, 800°-1300°, the carbon produced by the decomposition of

CO is in the form of lamp black, regardless of the form of carbon present in the reaction tube, viz: charcoal, coke, or coal. At any one temperature, therefore, k_2 should be the same in all three cases. From a comparison of tables 1-6, 11-15 and 16-18 it will be seen that there is considerable deviation in the values of k_2 for the three forms of carbon used. This is doubtless due in part to experimental errors. There is a further consideration, however, to which attention should be called, viz: that the reaction in question is not reversible. The lamp black produced by the reverse reaction



is not identical physically with the form of carbon, charcoal, or coke that is consumed in the formation of CO. Consequently the law of chemical mass action is not strictly applicable. In the systems under consideration, equilibrium would not be reached until all the carbon has been transformed to lamp black.

TABLE 20

VARIATION OF k_1 WITH TEMPERATURE (COKE)

$$\ln k_1 = -\frac{47220}{T} - 0.009699 T + 45.597$$

Temp. C.	T	k_1 (obs)	k_1 (calc)
900	1173	0.0024	0.0023
1000	1273	0.021	0.023
1100	1373	0.121	0.134
1200	1473	0.473	0.410
1300	1573	1.38	1.48

TABLE 21

VARIATION OF k_1 WITH TEMPERATURE (ANTHRACITE COAL)

$$\ln k_1 = \frac{31972}{T} + 0.02272 T - 56.607$$

Temp. C.	T	k_1
1100	1373	0.119
1200	1473	0.237
1300	1573	0.579

IX. APPLICATION OF EXPERIMENTAL RESULTS TO THE PROCESSES OF THE GAS PRODUCER AND BOILER FURNACE.

As stated in the introduction, the experiments here described were undertaken primarily to determine the temperature necessary for the formation of high percentage CO gas in the fuel bed of the gas producer, and to ascertain the conditions that govern the formation of CO in boiler furnaces. The results here presented indicate that the amount of CO formed in the gas producer depends on three factors: (1) the temperature; (2) the depth of the hot portion of the bed; and (3) the rate of flow of gas through the bed. Stated in a more concise form, the percentage of CO formed depends on the temperature and the time of contact of gas and carbon, i. e., the average time required for a molecule of gas to pass through the fuel bed. The variation of the percentage of CO with the rate of flow of gas is illustrated in Fig. 4, 6 and 7. The curves for coke, Fig. 6, may be taken as representing the conditions in the fuel bed of the producer. At 1300° C., for example, with zero velocity (time of contact = ∞)

practically all the CO₂ will be converted to CO; when $\frac{1}{t} = 0.5$, (time of contact $t = 2$ sec.), 90 per cent CO is obtained; and when $t = 1$ only 80 per cent CO is formed. In a fuel bed one foot in depth, since

$$\frac{1}{t} = \frac{\text{velocity of gas}}{\text{depth of fuel bed}} = \frac{v}{l}$$

a time of contact of $t = 2$ sec. corresponds to a velocity 0.5 ft. per sec. and $t = 1$ to a velocity of 1 ft. per sec. At 1300° C., then, in a fuel bed one foot in depth, with a velocity of 0.5 ft. per sec. 90 per cent of CO would be formed and with a velocity of 1 ft. per sec. 80 per cent. In a fuel bed two feet in depth, the gas velocities corresponding to the same percentage of CO would be twice as great. In other words, for given conditions of temperature and quality of gas, the depth of bed and velocity of gas

must vary proportionally and their ratio $\frac{v}{l}$ must remain constant. A fuel bed one foot in depth and a gas velocity of one foot per second should yield the same percentage of CO as a bed two feet in depth with a gas velocity of 2 ft. per sec.

It is impossible to determine accurately the velocity of the gas through the producer fuel bed, on account of the difficulty of estimating the magnitude of the passages through the bed.¹ The velocity lies probably between 0.5 and 5.0 ft. per sec. The right half of the curves in Fig. 6 lies within these limits and therefore corresponds approximately to the conditions of producer operation.

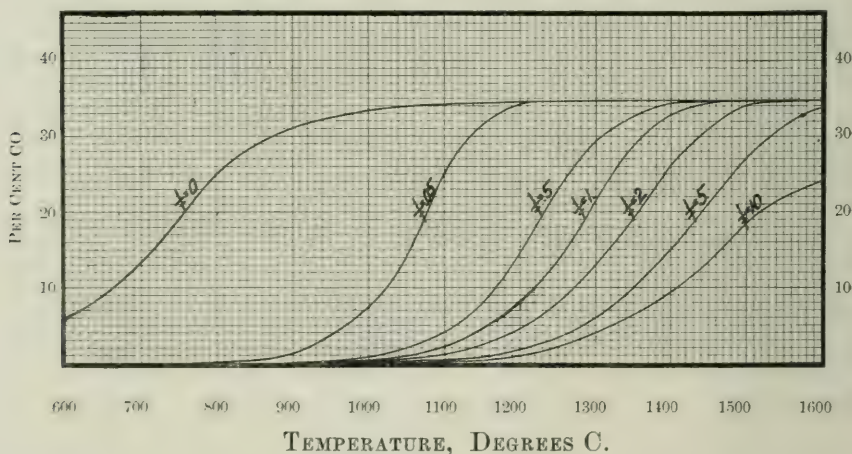


FIG. 8.

In Fig. 8 is shown graphically the variation with temperature of the amount of CO formed with different values of $\frac{1}{l}$. The

¹When any given number of pounds of air is passed per second through a fuel bed of given dimensions, the velocity through the bed will increase as the percentage of voids is decreased. Thus the velocity will be much higher with slack coal than with uniformly sized nut coal. Further, the per cent of voids will be influenced by the amount of coking and clinkering.

ordinate is the per cent of CO in gas containing initially 21 per cent CO_2 (air in which the oxygen has been converted quantitatively to CO_2). The abscissa is temperature in degrees Centigrade.

The upper curve, $\frac{1}{t} = 0$, represents the maximum amount of

CO which could be produced from air. The intersection of the curve for any velocity with a given horizontal line, for example, the line for $\text{CO} = 30$ per cent, gives the temperature required to form that amount of CO with the particular velocity. Thus to obtain 30 per cent CO with a velocity of one foot per sec. (length of bed = 1 ft.) will require a temperature of 1360°C ., and with a velocity of 2 ft. per sec., 1435° . The curves of Fig. 6 and 8 indicate that the temperature of the producer bed should not be less than 1300°C .

These investigations demonstrate that a very high temperature is necessary for the production of CO from CO_2 and carbon. There are other considerations, however, which are opposed to the operation of the fuel bed of the gas producer at extremely high temperature—above 1300°C .: A high temperature of fuel bed means that the gases will leave the producer at a high temperature and thus lower the efficiency of the producer. The gain in capacity will therefore be accompanied by a loss in efficiency, unless the heat of the gases can be used efficiently for generating steam and preheating the air blast. Also a high temperature favors clinkering. In the application of the results of these experiments to commercial producers and furnaces it will be necessary of course to consider the various questions that are involved.

Various explanations have been suggested to account for the presence of small amounts of carbon monoxide in the flue gases of boiler furnaces. Perhaps the one most generally accepted by engineers is that the oxygen of the air first unites with carbon to form CO_2 and that as this gas passes up through the hot fuel bed it combines with carbon in accordance with the equation



Assuming this to be the correct explanation, then the question to be solved is what conditions are favorable to this reaction and what conditions will tend to retard it. In the preceding paragraphs it has been shown that the higher the velocity of the gas and thinner the fuel bed, the less will be the percentage of CO formed. A heavy fuel bed in the boiler furnace would therefore favor the formation of CO. Also, the greater the supply of air to a given depth of bed, the less should be the tendency to form CO.

X SUMMARY AND CONCLUSIONS.

1. The rate of formation of CO in the reaction,



has been determined with charcoal from 800° to 1100° C., with coke from 900° to 1300° C., and with anthracite coal from 1100° to 1300° C.

2. The differential equation for the velocity of incomplete reactions

$$\frac{dx}{dt} = k_1 \left(a - \frac{a+1}{2} x \right) - k'_2 x^2$$

has been solved for given values of k'_2 and k_1 , and it has been shown (in the appendix) that the method is applicable to other cases.

3. Van't Hoff's laws for the variation of equilibrium constants and coefficients of reaction velocity with temperature have been applied to the values of k_1 and K obtained in these experiments, and a close agreement between observed and calculated values has been found.

4. By means of the equations expressing the laws referred to in paragraphs (2) and (3) it is possible to compute the percentage of CO formed at any temperature and with any time of contact.

5. It has been shown that for the production of a high percentage of CO gas, the producer fuel bed should have a temperature of 1300° C. or over, and that increasing the depth of the hot

portion of the bed will increase the percentage of CO, and consequently the capacity of producer at first rapidly and then more and more slowly.

6. To minimize the production of CO in the boiler furnace the fuel bed should be thin. Increasing the velocity of the gas will tend to decrease rather than increase the percentage of CO formed.

APPENDIX

ON THE COMPUTATION OF THE CONSTANTS OF THE REACTION
EQUATION

BY CHARLES N. HASKINS.

1. REDUCTION AND INTEGRATION OF THE DIFFERENTIAL EQUATION.

The differential equation is

$$\frac{dx}{dt} = k_1 \left(a - \frac{a+1}{2} x \right) - k_2 x^2,$$

where $100 a = \% (\text{CO} + \text{CO}_2) \text{ at time } t = 0,$ (1)

$100 x = \% \text{ CO at time } t,$

$t = \text{time in seconds},$

and k_1 and k_2 are the two constants of the reaction the values of which are sought. The initial condition is that

$$x = 0, \text{ when } t = 0. \quad (2)$$

To integrate, we introduce a new variable z and new constants α, γ , defined by the relations

$$\left. \begin{aligned} z &= \frac{\left(\frac{a+1}{2}\right) x}{2a - \left(\frac{a+1}{2}\right) x}, & x &= \frac{2 a z}{\left(\frac{a+1}{2}\right)(1+z)}, \\ \alpha &= \frac{1}{2} \left(\frac{a+1}{2}\right) k_1 \sqrt{1 + \left(\frac{2}{a+1}\right)^2 \frac{4a k_2}{k_1}}, & k_1 &= \frac{2 a \gamma}{\left(\frac{a+1}{2}\right)}, \\ r &= \frac{1}{\sqrt{1 + \left(\frac{2}{a+1}\right)^2 \frac{4a k_2}{k_1}}}, & k_2 &= \frac{1}{a} \left(\frac{a+1}{2}\right)^\alpha \frac{(1-r^2)}{2\gamma} \end{aligned} \right\} \quad (3)$$

The differential equation becomes, under these substitutions,

$$\frac{dz}{dt} = \frac{a}{\gamma}(\gamma^2 - z^2) \quad (4)$$

with the initial condition $z = 0$, when $t = 0$. (5)

Integrating, we have

$$\ln \frac{\gamma + z}{\gamma - z} = 2 at; \quad (6)$$

and solving for z ,

$$z = \gamma \frac{e^{at} - e^{-at}}{e^{at} + e^{-at}} = \gamma \tanh at; \quad (7)$$

whence, substituting in (3),

$$x = \frac{2 a \gamma \tanh at}{\left(\frac{a+1}{2}\right)(1 + \gamma \tanh at)}. \quad (8)$$

2. THE EQUATION FOR γ AND THE CRITERION FOR THE EXISTENCE OF ONE AND ONLY ONE ROOT.

We have (equation 8) an expression by means of which the per cent of CO at any time t may be computed if the constants γ and a are known. We now wish to determine γ and a from two pairs of observed corresponding values of t and x . Let these two pairs be (t_1, x) , and (t_2, x_2) , and let $t_2 > t_1$.

Then since a is known we may compute

$$z_1 = \frac{\left(\frac{a+1}{2}\right) x_1}{2a - \left(\frac{a+1}{2}\right) x_1}, \quad z_2 = \frac{\left(\frac{a+1}{2}\right) x_2}{2a - \left(\frac{a+1}{2}\right) x_2};$$

and have

$$\ln \frac{\gamma + z_1}{\gamma - z_1} = 2 at_1, \quad \ln \frac{\gamma + z_2}{\gamma - z_2} = 2 at_2, \quad (9)$$

from which γ and a are to be determined. Eliminating a , we readily obtain

$$\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1}. \quad (10)$$

The symbols $\ln x$, $\log x$ will be used to denote the natural and the common logarithm of x , respectively.

The determination of γ and α depends therefore on the solution of this (transcendental) equation in γ .

Consideration of the function

$$U(\gamma) \equiv t_1 \ln \frac{\gamma + z_2}{\gamma - z_2} - t_2 \ln \frac{\gamma + z_1}{\gamma - z_1}, \quad (11)$$

and of its derivative

$$U'(\gamma) \equiv -2 \left(\frac{t_1 z_2}{\gamma^2 - z_2^2} - \frac{t_2 z_1}{\gamma^2 - z_1^2} \right) \quad (12)$$

shows that the equation

$$\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1} \quad (10)$$

has a root $\gamma > z_2$ when and only when

$$t_2 z_1 - t_1 z_2 > 0, \text{ that is, } \frac{z_2}{z_1} < \frac{t_2}{t_1}. \quad (13)$$

If a root exists there is but one, and it satisfies the inequalities

$$z_2 < \gamma < \sqrt{z_1 z_2 - \frac{(t_2 z_2 - t_1 z_1)}{t_2 z_1 - t_1 z_2}}. \quad (14)$$

The inequality (13) furnishes a negative criterion for the applicability of the differential equation (1) to a reaction under investigation. For if the reaction is governed by equation (1) and if the observations are made with sufficient accuracy there must exist a γ satisfying equation (10) and hence the inequality (13) must be satisfied. If, then, this inequality is not satisfied, and hence no such γ can be found; then either the assumptions involved in (1) must be invalid, or there must be errors in the observations. On the other hand, if (13) is satisfied we can only conclude that (1) *may* be applicable, and we proceed to determine whether it is so by computing γ and α and comparing the values of x computed by means of (8) with the observed values of x .

3. SOLUTION OF THE EQUATION $\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1}$.

If the selected pairs $(t_1, x_1), (t_2, x_2)$ of observed values satisfy the criterion

$$\frac{z_2}{z_1} < \frac{t_2}{t_1} \quad (13)$$

we compute γ as follows. Passing, for convenience of computation, from natural to common logarithms, we have

$$\log \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \log \frac{\gamma + z_1}{\gamma - z_1}. \quad (10a)$$

Assume now a value for γ , say $\gamma = \gamma_1$,

where
$$z_2 < \gamma_1 < \sqrt{z_1 z_2 \frac{(t_2 z_2 - t_1 z_1)}{t_2 z_1 - t_1 z_2}}.$$

Then we may compute a quantity $\log N_1$ by the equation

$$\log N_1 = \frac{t_2}{t_1} \log \frac{\gamma + z_1}{\gamma - z_1}, \quad (15)$$

Determine now a new value of γ , $\gamma = \gamma_2$, by the relation

$$\log \frac{\gamma_2 + z_2}{\gamma_2 - z_2} = \log N_1 \quad (16)$$

that is,

$$\frac{\gamma_2 + z_2}{\gamma_2 - z_2} = N_1 \quad (16a)$$

or¹

$$\gamma_2 = z_2 \frac{N_1 + 1}{N_1 - 1}. \quad (16b)$$

Proceed now to determine a new approximation γ_3 from γ_2 in the same way that γ_2 was determined from γ_1 , and continue the process until its repetition produces either no change, or a change which is negligible compared with the experimental errors. It will be found that in general the process converges fairly rapidly and only a few repetitions are necessary.

¹This computation may be abridged by the use of Gaussian logarithms.

Suppose, then, that γ has been found by this process. Then α is computed by either of the relations

$$2 \alpha = \frac{1}{t_2} \ln \frac{\gamma + z_1}{\gamma - z_1}, \quad 2 \alpha = \frac{1}{t_1} \ln \frac{\gamma + z_2}{\gamma - z_2} \quad (9a)$$

or, what amounts to the same thing, if N is the last of the numbers $N_1, N_2, \dots$ used in computing γ ,

$$2 \alpha = \frac{1}{t_2} \ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{1}{t_2} \ln N = \frac{1}{t_2} \log N \cdot \ln 10, \quad (17)$$

$$2 \alpha = \frac{2.3026}{t_2} \log N.$$

4. COMPUTATION OF THE REACTION-CONSTANTS k_1 , k_2 , AND VERIFICATION OF THE REACTION-EQUATION.

When the constants α , γ have been computed we can find the original constants k_1 , k_2 by the relations

$$k_1 = \frac{2 \alpha \gamma}{\left(\frac{\alpha + 1}{2}\right)}, \quad k_2 = \frac{1}{\alpha} \left(\frac{\alpha + 1}{2}\right) \frac{(1 - \gamma^2)}{\gamma}. \quad (3)$$

To determine the applicability of the reaction-equation (1) to the case in hand, we have now only to introduce the values α , γ , just found into the equation

$$z = \gamma \tanh \alpha t, \quad (7)$$

$$x = \frac{2 \alpha \gamma \tanh \alpha t}{\left(\frac{\alpha + 1}{2}\right) \left(1 + \gamma \tanh \alpha t\right)} \quad (8)$$

and compare the values of z or x obtained with those found by observation. For this purpose equation (7) is the simpler, especially when the z 's corresponding to observed values of x have already been computed.

5. CORRECTION OF THE CONSTANTS a , γ BY THE METHOD OF LEAST SQUARES.

The constants a , γ obtained above are determined by two pairs of observations only. It is of course desirable that all the observations be used in fixing their values, as on account of experimental errors the values obtained from different pairs of observations will in general not be identical. We proceed, therefore, to correct the constants by the Method of Least Squares.

Let $(t_1, x_1); (t_2, x_2); \dots (t_n, x_n)$ be n observed pairs of values of t and x . The problem is then to determine a and γ in such a way that if

$$\ln \left(\frac{\gamma + z_i}{\gamma - z_i} \right) - 2 a t_i \equiv \delta_i \quad (6^1)$$

then

$$n\delta^2 \equiv \sum_1^n \delta_i^2 \quad (18)$$

shall be a minimum.

In order that a and γ shall make $n\delta^2$ a minimum they must satisfy the so-called normal equations:

$$\begin{aligned} \frac{n}{2} \frac{d(\delta^2)}{da} &\equiv \sum_1^n \delta_i \frac{d\delta_i}{da} \equiv \sum_1^n 2 t_i \left\{ 2 a t_i - \ln \left(\frac{\gamma + z_i}{\gamma - z_i} \right) \right\} = 0, \\ \frac{n}{2} \frac{d(\delta^2)}{d\gamma} &\equiv \sum_1^n \delta_i \frac{d\delta_i}{d\gamma} \equiv \\ \sum_1^n \left\{ \frac{1}{\gamma + z_i} - \frac{1}{\gamma - z_i} \right\} \left\{ \ln \left(\frac{\gamma + z_i}{\gamma - z_i} \right) - 2 a t_i \right\} &= 0. \end{aligned} \quad (19)$$

These equations may be written

$$\begin{aligned} 2 a \sum_1^n t_i^2 + \sum_1^n t_i \ln \left(\frac{\gamma - z_i}{\gamma + z_i} \right) &= 0, \\ 2 a \sum_1^n \frac{t_i z_i}{\gamma^2 - z_i^2} + \sum_1^n \frac{z_i}{\gamma^2 - z_i^2} \ln \left(\frac{\gamma - z_i}{\gamma + z_i} \right) &= 0. \end{aligned} \quad (20)$$

As their exact solution in their present form is impracticable on account of their complexity we replace them in the usual way by a system of approximately equivalent linear equations, by making use of the fact that the quantities u, v by which a and γ differ from a_0, γ_0 respectively are small compared with a_0, γ_0 .

Substituting

$$\begin{aligned} a &= a_0 + u \\ \gamma &= \gamma_0 + v, \end{aligned} \quad (21)$$

we have

$$\begin{aligned} 2u \sum_1^n t_i^2 + \sum_1^n t_i \ln \left(\frac{1 + \frac{v}{\gamma_0 - z_i}}{1 + \frac{v}{\gamma_0 + z_i}} \right) &= \sum_1^n t_i \left\{ \ln \left(\frac{\gamma_0 + z_i}{\gamma_0 - z_i} \right) - 2at_i \right\} \\ &\quad + \sum_1^n t_i \ln \left(\frac{1 + \frac{v}{\gamma_0 - z_i}}{1 + \frac{v}{\gamma_0 + z_i}} \right) \quad (22) \\ 2u \sum_1^n \frac{t_i z_i}{(\gamma_0^2 - z_i^2) \left(1 + \frac{2\gamma_0 v + v^2}{\gamma_0^2 - z_i^2} \right)} + \sum_1^n \frac{z_i \ln \left(\frac{\gamma_0 + z_i}{\gamma_0 - z_i} \right)}{(\gamma_0^2 - z_i^2) \left(1 + \frac{2\gamma_0 v + v^2}{\gamma_0^2 - z_i^2} \right)} \\ &= \sum_1^n \frac{z_i \left\{ \ln \left(\frac{\gamma_0 + z_i}{\gamma_0 - z_i} \right) - 2a_0 t_i \right\}}{(\gamma_0^2 - z_i^2) \left(1 + \frac{2\gamma_0 v + v^2}{\gamma_0^2 - z_i^2} \right)}. \end{aligned}$$

Expanding the logarithms by Maclaurin's series and neglecting terms of the order of uv and v^2 in comparison with those of the order of u and v we have

$$\begin{aligned} u \sum_1^n t_i^2 + v \sum_1^n \frac{t_i z_i}{\gamma_0^2 - z_i^2} &= \sum_1^n \frac{t_i}{2} \left(\ln \frac{\gamma_0 + z_i}{\gamma_0 - z_i} - 2a_0 t_i \right) \\ u \sum_1^n \frac{t_i z_i}{\gamma_0^2 - z_i^2} + v \sum_1^n \frac{z_i^2}{(\gamma_0^2 - z_i^2)} &= \sum_1^n \frac{z_i}{(\gamma_0^2 - z_i^2)} \left(\ln \frac{\gamma_0 + z_i}{\gamma_0 - z_i} - 2a_0 t_i \right) \end{aligned} \quad (23)$$

Expressing the natural logarithms in terms of common logarithms we have, putting

$$A_i \equiv t_i, \quad B_i \equiv \frac{z_i}{\gamma_0^2 - z_i^2}, \quad C_i \equiv \log \frac{\gamma_0 + z_i}{\gamma_0 - z_i} - M t_i,$$

$$K \equiv \frac{\ln 10}{2} \equiv 1.15129, \quad M \equiv \frac{2a_0}{\ln 10} \equiv 0.86859 a_0;$$

$$u \sum_1^n A_i^2 + v \sum_1^n A_i B_i = K \sum_1^n A_i C_i, \quad (24)$$

$$u \sum_1^n B_i A_i + v \sum_1^n B_i^2 = K \sum_1^n B_i C_i, \quad (25)$$

or in the usual notation of the method of least squares

$$\begin{aligned} u [A A] + v [A B] &= K [A C], \\ u [B A] + v [B B] &= K [B C]. \end{aligned} \quad (26)$$

From these equations u and v are readily computed and hence the corrected values

$$\begin{aligned} \gamma &= a_0 + u \\ \gamma &= a_0 + v \end{aligned} \quad (21)$$

are found.

6. APPLICATION OF THE METHOD OF §§ 3, 4 TO OTHER EQUATIONS OF REACTION-VELOCITY.

The well known equation¹

$$\frac{dx}{dt} = k_1 (1 - x)^2 - k_2 x^2, \quad (27)$$

with the initial condition $x = 0$, when $t = 0$, is reducible by the substitutions

$$\left. \begin{aligned} z &= \frac{x}{1-x}, & x &= \frac{z}{1+z}, \\ a &= \sqrt{k_1 k_2}, & k_1 &= a \gamma, \\ \gamma &= \sqrt{\frac{k_1}{k_2}}, & k_2 &= \frac{a}{\gamma}, \end{aligned} \right\} \quad (28)$$

to the form we have considered, viz.:

¹Cf Nernst, *Theoretische Chemie*, 5 Aufl, p. 564; 2d English edition, p. 568.

$$\frac{dz}{dt} = \frac{a}{\gamma} (\gamma^2 - z^2) \quad (4)$$

with the initial condition $z = 0$ when $t = 0$. Its integral is, therefore,

$$\ln \frac{\gamma + z}{\gamma - z} = 2at, \quad (6)$$

or
$$z = \gamma \tanh at, \quad (7)$$

or
$$x = \frac{\gamma \tanh at}{1 + \gamma \tanh at}, \quad (8)$$

and the constants are determined by the equation

$$\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1} \quad (10)$$

if the criterion

$$\frac{z_2}{z_1} < \frac{t_2}{t_1} \quad (13)$$

is satisfied.

The more general equation¹

$$\frac{dx}{dt} = k_1 (a_1 - x) (b_1 - x) - k_2 (a_2 + x) (b_2 + x), \quad (29)$$

with initial conditions $x = 0$, when $t = 0$ is reducible by a substitution of the form

$$x = \frac{\rho z - \sigma}{1 + z}. \quad (30)$$

where ρ and σ are constants depending on a_1, b_1, a_2, b_2 but not on k_1, k_2 , to the equation

$$\frac{dz}{dt} = \frac{a}{\gamma} (\gamma^2 - z^2). \quad (4)$$

The initial conditions, however, are now not

$$t = 0, z = 0, \quad (5)$$

but
$$t = 0, z = \frac{\sigma}{\rho} \equiv z_0; \quad (5')$$

and hence the integral and the equation determining the constants are more complicated.

¹Cf. Nernst, *Theoretische Chemie*. 5 Aufl. p. 543; 2d English edition, p. 542.

The equation determining γ is

$$\ln \frac{\gamma + z_2}{\gamma - z_2} = \frac{t_2}{t_1} \ln \frac{\gamma + z_1}{\gamma - z_1} - \left(\frac{t_2}{t_1} - 1 \right) \ln \frac{\gamma + z_0}{\gamma - z_0} \quad (31)$$

and the criterion for the existence of a solution is

$$t_2 z_1 - t_1 z_2 - (t_2 - t_1) z_0 > 0. \quad (32)$$

The solution, if existent, is unique, and is determined by a process similar to that of § 3.

7. CONCLUSION.

The analysis in the preceding sections furnishes a simple negative criterion (13) or (32) for the applicability of the differential equation (1) or (29) to a given reaction and, in case this criterion is satisfied, provides a straightforward method of computing the numerical values of the reaction constants k_1 and k_2 from *any* two pairs of observed corresponding values of x and t . It renders unnecessary, moreover, except as a matter of control, any observations of equilibrium conditions.

The detailed discussion of the more general equation (29) is reserved for subsequent publication.

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